

Non-rigid shell model and novel correlational effects in atomic and molecular systems

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Abstract

Direct analytical and numerical calculation show that two-electron atomic configuration can be unstable with respect to a static or dynamic shift of the electron shells. This enables to develop a so called non-rigid shell model for a partial account of the electron correlations within atomic clusters in solids. In a framework of this model a correlated state of two-electron molecular configuration is described by a set of symmetrized shell shifts q^γ similarly to the well known shell model developed for a description of the lattice dynamics. A set of q^γ -shifts are found after minimization of the energy functional. We present a number of the novel unconventional effects including: i) a correlational mechanism of the local pairing; ii) a correlational (pseudo) Jahn-Teller effect provided by a joint account of the electron shell shifts and conventional nuclear displacements; iii) an appearance of the chiral correlational states. The model allows an introduction of the pseudo-spin formalism and effective "spin-Hamiltonian" for a description of the short- and long-range ordering of non-rigid atomic backgrounds in crystals. Finally, the model can be readily built in the conventional band schemes.

1 Introduction

Electronic correlations is one of the fundamental problem in a theory of atoms, molecules and solid state, particularly for the systems with high density of excited states when a small perturbation can result both in drastic reconstruction of the energy spectrum and in modification of the ground state up to formation of a strongly correlated state. As a rule, in such a situation an appropriate description of the ground state within the bare restricted basis often requires a lot of configurations or considerable extension of the basis, and so becomes difficult for practical realization and interpretation. Namely this situation occurs in atoms, where description of some specific correlation effects in terms of Hartree-Fock basis requires a large number of Hartree-Fock configurations.

Such a problem implies a search for alternative variational approaches to the electronic structure and energy spectrum.

In this work we develop further the variational method for the many-electron atomic clusters with the trial parameters being the coordinates of the center of the one-particle atomic orbital [1]. The resulting shift of the atomic orbital allows to interpret the variation of the electronic density distribution rather clearly, and the symmetry of a system can be readily used for construction of the trial many-electron wave function. The shifted electronic shells in conventional MO-LCAO-scheme with restricted set of the one-particle states allow to take into account an additional multipole interactions and to construct novel states with unique properties. As a whole the model bears a strong resemblance to the well known shell model widely used in lattice dynamics.

2 Two-electron configuration

We consider the problem of two electrons in certain atomic potential to be a simplest model for manifestation of electronic correlations. The orbital part of the singlet two-electron wave function formed by the shifted one-particle orbitals (bi-orbital) can be written as follows:

$$\Psi(\vec{r}_1, \vec{r}_2; \vec{\alpha}, \vec{\beta}) = \eta^{-1} [\psi(\vec{r}_1 - \vec{\alpha}) \psi(\vec{r}_2 - \vec{\beta}) + \psi(\vec{r}_1 - \vec{\beta}) \psi(\vec{r}_2 - \vec{\alpha})], \quad (1)$$

where $\vec{\alpha}, \vec{\beta}$ are the displacement vectors for the one-particle orbitals (Fig.1), η the normalization factor. Below, only the real functions of s -type are used as the trial one-particle states. Then

$$\eta^2 = 2 \left(1 + S^2(\vec{\alpha}, \vec{\beta}) \right), \quad (2)$$

where $S(\vec{\alpha}, \vec{\beta})$ is the overlap integral for the one-particle orbitals. The Hamiltonian of the problem in atomic units ($\epsilon_0 = \frac{me^4}{\hbar^2} = \frac{e^2}{a_0}$, $a_0 = \frac{\hbar^2}{me^2}$) is

$$\hat{H} = -\frac{\Delta_1}{2} - \frac{\Delta_2}{2} - \frac{Z_0}{r_1} - \frac{Z_0}{r_2} + \frac{1}{|\vec{r}_1 - \vec{r}_2|}. \quad (3)$$

The variational procedure is performed with the full energy functional:

$$E\{\Psi\} \equiv \langle \Psi | \hat{H} | \Psi \rangle = E(\vec{\alpha}, \vec{\beta}). \quad (4)$$

Taking into account the expression (1) we obtain:

$$E(\vec{\alpha}, \vec{\beta}) = \frac{1}{1 + S^2(\vec{\alpha}, \vec{\beta})} [2 t(\vec{\alpha}, \vec{\alpha}) - Z_0 (u(\vec{\alpha}, \vec{\alpha}) + u(\vec{\beta}, \vec{\beta})) + 2 S(\vec{\alpha}, \vec{\beta}) t(\vec{\alpha}, \vec{\beta}) - 2 Z_0 S(\vec{\alpha}, \vec{\beta}) u(\vec{\alpha}, \vec{\beta}) + c(\vec{\alpha}, \vec{\beta}) + a(\vec{\alpha}, \vec{\beta})], \quad (5)$$

where the following matrix elements are introduced: the one-center integral $t(\vec{\alpha}, \vec{\alpha})$ is the kinetic energy of an electron with functions of the same center, the two-center integral $u(\vec{\alpha}, \vec{\alpha})$ is the interaction of an electron with the potential center with functions of the same center, the two-center integral $t(\vec{\alpha}, \vec{\beta})$ is the kinetic energy of an electron with functions of different centers, the three-center integral $u(\vec{\alpha}, \vec{\beta})$ is the interaction of an electron with the potential center with functions of different centers, $c(\vec{\alpha}, \vec{\beta})$ and $a(\vec{\alpha}, \vec{\beta})$ are the Coulomb and the exchange parts of the inter-electron interaction. One should note that $S(\vec{\alpha}, \vec{\beta})$, $c(\vec{\alpha}, \vec{\beta})$, $a(\vec{\alpha}, \vec{\beta})$ are the two-center integrals.

In further we use the Slater functions with the index k and effective charge Z as the one-particle atomic orbitals:

$$\psi(\vec{r}) = N_{Z,k} r^k e^{-Zr}, \quad (6)$$

where the normalization factor is

$$N_{Z,k} = \sqrt{\frac{Z}{2\pi (2k+2)!}} (2Z)^{k+1}. \quad (7)$$

The analytic expressions for the matrix elements are presented in Appendix. Their examination allows to obtain some information about extremal values of the $\vec{\alpha}$ and $\vec{\beta}$. Introducing

$$\vec{q}_+ = \frac{1}{2} (\vec{\alpha} + \vec{\beta}), \vec{q}_- = \frac{1}{2} (\vec{\alpha} - \vec{\beta}) \quad (8)$$

and the coordinate system with center at $\vec{q}_+ = 0$, one can see that only $u(\vec{\alpha}, \vec{\alpha}) + u(\vec{\beta}, \vec{\beta})$, $u(\vec{\alpha}, \vec{\beta})$ depend on \vec{q}_+ :

$$u(\vec{\alpha}, \vec{\alpha}) + u(\vec{\beta}, \vec{\beta}) = \int \frac{d\vec{r}}{|\vec{r} - \vec{q}_+|} (\psi^2(\vec{r} - \vec{q}_-) + \psi^2(\vec{r} + \vec{q}_-)), \quad (9)$$

$$u(\vec{\alpha}, \vec{\beta}) = \int \frac{d\vec{r}}{|\vec{r} - \vec{q}_+|} \psi(\vec{r} - \vec{q}_-) \psi(\vec{r} + \vec{q}_-).$$

These quantities are invariants with respect to inversion in the displacement vector space, hence $\vec{q}_+ = 0$ is a critical point in \vec{q}_+ -space. The surface $E\{\Psi\} = \text{const}$ in \vec{q}_+ -space is a sphere for the one-particle s -functions, and the point $\vec{q}_+ = 0$ is a minimum or a maximum. In general, for an arbitrary angular

dependence of the one-particle functions ψ the point $\vec{q}_+ = 0$ can be also a saddle point.

It is rather clear, why the point $\vec{q}_+ = 0$ appears to be critical: at the given value of the interaction with the potential center, the configuration with $\vec{\alpha} = -\vec{\beta}$ can minimize inter-electron repulsion. This is confirmed by results of numerical minimization of the full energy functional for the $1s^2$ -configuration ($k = 0$) which are listed in the Table 1 and 2. Thus, the following function can be defined

$$\Psi(\vec{r}_1, \vec{r}_2; \vec{q}) = \eta^{-1} [\psi(\vec{r}_1 - \vec{q}) \psi(\vec{r}_2 + \vec{q}) + \psi(\vec{r}_1 + \vec{q}) \psi(\vec{r}_2 - \vec{q})], \quad (10)$$

that leads to the reduction of the number of trial parameters. The full energy functional with functions $\psi(r)$ (6) depends only on the $q = |\vec{q}|$, but not on the direction of \vec{q} .

The value Z in the calculations mentioned above was a free parameter. This parameter provides an additional mechanism of the electronic density redistribution along with the electronic shell shift. For the isolated atom it is naturally to assume that Z is also the variational parameter, because in this situation the atomic potential is the only mechanism of the electronic density redistribution:

$$E\{\Psi\} = E(q, Z) \equiv E(\vec{\alpha} = \vec{q}, \vec{\beta} = -\vec{q}; Z) \quad (11)$$

It should be noted that in a crystal the functions with certain "atomic" value Z which minimizes the energy of the isolated atom can form the strongly correlated state like shifted electronic shell state for the minimization of given crystal potential characterized by the parameter Z_0 .

3 Expansion of the full energy functional

The function (10) possess the following property: it has no linear term in the q -expansion at $q = 0$. As

$$\frac{\partial \psi(\vec{r} - \vec{q})}{\partial q} \Big|_{q=0} = - \frac{\partial \psi(\vec{r} + \vec{q})}{\partial q} \Big|_{q=0}, \quad (12)$$

the first derivative of the function (10) at $q = 0$ turns to zero. Hence, the $E(q, Z)$ with the functions (10) has an extremum at $q = 0$, which type is defined by sign of the quadratic term $E^{(2)}$ in the q -expansion of the $E(q)$:

$$E(q) \approx E^{(0)} + E^{(2)} q^2. \quad (13)$$

For the functions (6) the full energy functional doesn't depend on the direction of \vec{q} , and therefore we consider shifts to be directed along z -axis. The q -expansion of the function (10) can be written in the following form:

$$\psi(\vec{r} - \vec{q}) \approx a(\vec{r}) - b(\vec{r}) q + \frac{1}{2} c(\vec{r}) q^2, \quad (14)$$

where

$$a(\vec{r}) = \psi(\vec{r} - \vec{q})|_{q=0} = N_{Z,k} r^k e^{-Zr}, \quad (15)$$

$$b(\vec{r}) = \frac{\partial \psi(\vec{r} - \vec{q})}{\partial z}|_{q=0} = N_{Z,k} (k r^{k-1} - Z r^k) e^{-Zr} \cos \theta, \quad (16)$$

$$c(\vec{r}) = \frac{\partial^2 \psi(\vec{r} - \vec{q})}{\partial^2 z}|_{q=0} = N_{Z,k} [k r^{k-2} - Z r^{k-1} + \\ + (k(k-2) r^{k-2} - Z(2k-1) r^{k-1} + Z^2 r^k) \cos^2 \theta] e^{-Zr}, \quad (17)$$

with the angle θ counted out from z -axis. The q -expansion of the matrix elements up to quadratic terms and the expressions for $E^{(0)}$ and $E^{(2)}$ are listed in the Table 3.

From the expression for $E^{(2)}$ the criterion of the non-zero shift of the electronic shell can be obtained for the $1s$ -function ($k = 0$) as the one-particle state. The shift is not zero, if $Z > Z_0 - \frac{3}{16}$; in opposite case there is no displacement of the electronic shell from the potential center. This result is entirely compatible with our numerical calculations presented in Table 2. The minimum of $E(Z, q)$ for $k = 0$ is obtained for $q_{min} = 0$ and $Z_{min} = Z_0 - \frac{5}{16}$, that agrees with the well-known result in the helium atom theory [3].

From the other hand, the full energy functional with functions (10) formed from the one-particle ns -states (6) with $k \neq 0$ has the minimum at $q \neq 0$ for any values Z_0 and Z . It means that for these states the non-zero shift of the electronic shell always takes place.

The expression for $E^{(0)}$ allows to find the value of the effective charge Z that minimizes full energy of the ns^2 -configuration at $q = 0$:

$$Z_{min} = Z_0 \frac{2k+1}{k+1} - \left(\frac{2k+1}{2k+2} - \frac{(2k+1)(4k+3)!}{2^{4k+3} [(2k+2)!]^2} \right). \quad (18)$$

At $k \rightarrow \infty$ this expression tends to $Z_{min}^\infty = 2Z_0 - 1$.

Origin of the different behaviour of the electronic shells with $k = 0$ and $k \neq 0$ can be readily understood from the data listed in Table 3. The principal difference of the one-particle function with $k \neq 0$ from that of with $k = 0$ is

that the function with $k \neq 0$ turns into zero at $r = 0$ (Fig.2). The energy of interaction of electrons with the potential center appears to be most sensitive to the electron density on nucleus. Its displacement leads to strong increase of the full energy of the system in the case of wave function with $k = 0$, and, from the other hand, zero density at $r = 0$ for the function with $k \neq 0$ provides specific "softness" of this part of interaction that is revealed in zero value of quadratic term in expansion of $u(\vec{q}, -\vec{q})$. The expressions for matrix element $t(\vec{q}, -\vec{q})$ describing relative motion of the electron shells are different at $k = 0$ and $k \neq 0$ whereas the overlap integrals $(S(\vec{q}, -\vec{q}), c(\vec{q}, -\vec{q}), a(\vec{q}, -\vec{q}))$ have the same structure for the both cases. Finally, it can be concluded that the gain in the electron-electron interaction at $k \neq 0$ with displacement of the electronic shells hasn't been compensated by the loss in the energy of interaction with the potential center as in the case $k = 0$.

An appearance of the electronic density on the potential center also implies the gain in energy. This makes possible to determine the most favorable directions of displacement of the electronic shells in the case of the anisotropic wave function with node at $r = 0$. So, for p_z -orbital it has to be z -axis direction, for $d_{x^2-y^2}$ -orbital the critical directions are along x - and y -axis, and so on. Finally, for the $k \neq 0$ orbitals one should expect a well developed non-trivial $q \neq 0$ minimum at the energy surface $E(q, Z)$. This conclusion appears to be compatible with the results of numerical minimization of the full energy functional for np^2 -configuration [4].

4 The form of the full energy functional $E(q, Z)$

The general expressions for the matrix elements in case of the electronic configuration with $\vec{\alpha} = \vec{q}$ and $\vec{\beta} = -\vec{q}$ can be obtained from those listed in Table 1 at $\rho = 2Zq$, $\tilde{\alpha} = Zq$ and with transition to the limit $\xi \rightarrow 0$, $\eta \rightarrow 0$ in expression for $u(\vec{\alpha}, \vec{\beta})$. In terms of $\rho = 2Zq$ the latter can be written as:

$$u(\vec{q}, -\vec{q}) = Z \frac{\rho^{2k+2}}{(2k+2)!} \sum_{s=0}^{k+1} (4s+1) b_0^{(s)} \Sigma_{s,0}^{(k+1)}(\rho). \quad (19)$$

At $k = 0$ the matrix elements coincide with the well-known fundamental results from the atomic theory [5,6].

The results of minimization of $E(q, Z)$ for a number of the lowest values of k ($k = 0, \dots, 4$) are listed in Table 4; the full energy functional as a function of q at $Z = Z_{min}^k$ is shown in Fig.3. As it was mentioned above, for $k \neq 0$ the displacement of the electronic shells takes place. The gain in energy is $0.22 \div 0.36 \text{ a.u.}$, and the value of displacement is $0.34 \div 0.76 \text{ a.u.}$ for $k = 1, \dots, 4$.

The k -dependence of the global minimum can be explained by the character of the electronic density distribution at different k . The Fig.2 shows that the increasing in k is accompanied by the lower values of the electronic density near $r = 0$. The gain in energy of a system can be provided by decreasing of electron-electron interaction (decreasing of positive contribution from $t(\vec{q}, -\vec{q})$, $c(\vec{q}, -\vec{q})$, $a(\vec{q}, -\vec{q})$) and by increasing of the interaction with the potential center (increasing of negative contribution from $u(\vec{q}, \vec{q})$, $u(\vec{q}, -\vec{q})$). The rising of q_{min} with the index k is associated with the delocalization $\psi_k(r)$; the lower value of the overlap and, therefore, the lower interaction of the electrons are obtained with rising of q . Another mechanism providing the overlap decrease is in increasing of Z , that leads also to a localization of $\psi(r)$ (see Fig.4). With increasing Z the negative contribution from interaction with the potential center and the positive ones from kinetic energy are increased simultaneously resulting in certain compromise value of Z . This value increases with k due to a delocalization of $\psi(r)$ with k . In Fig.5 the value q_{min} as function of Z is also shown.

5 The dynamic shifts of the electronic shells

The distribution of the electronic density at $k = 1$ with and without shifts is shown in Fig.6; in the both cases the wave functions providing the minimum of the full energy functional are used. The symmetry of the electronic density distribution with the shifts ($C_{\infty h}$) breaks the initial spherical symmetry, which can be restored with taking into account the energy equivalent configurations with various directions of the displacement vectors.

The full energy functional can have the continuum of the equivalent minima in the displacement vector space. In this sense the system has the variational degeneracy. The existence itself, the form and other parameters of the minima continuum depend on the one-particle states and the parameters of the potential. In the case of the ns^2 -configuration mentioned above, only the value of difference of the displacement vectors of the one-particle states is fixed $|\vec{\rho}| = |\vec{\alpha} - \vec{\beta}| = 2q$ (with $\vec{\alpha} = \vec{q}$, $\vec{\beta} = -\vec{q}$), so the continuum is a sphere in the \vec{q} space that restores the initial spherical symmetry of the system. By analogy with the description of collective motion in nuclei [7], one can form the linear combinations with a help of the bi-orbitals Ψ which have different vectors \vec{q}_{min} :

$$\tilde{\Psi}_f(\vec{r}_1, \vec{r}_2) = \int \Psi(\vec{r}_1, \vec{r}_2; \vec{q}, -\vec{q}) f(\Omega) d\Omega, \quad (20)$$

where integration is performed on a sphere in the \vec{q} space. Such a linear combination can provide the lower energy due to the "off-diagonal" in \vec{q} matrix elements of the full energy functional which take account of the "interaction"

of bi-orbitals. The variational procedure with the functions (20) yields an integral equation for the function $f(\Omega)$:

$$\int d\Omega f(\Omega) [K(\vec{q}, \vec{q}') - E \cdot I(\vec{q}, \vec{q}')] = 0, \quad (21)$$

where

$$K(\vec{q}, \vec{q}') = \langle \Psi(\vec{q}, -\vec{q}) | \hat{H} | \Psi(\vec{q}', -\vec{q}') \rangle$$

$$I(\vec{q}, \vec{q}') = \langle \Psi(\vec{q}, -\vec{q}) | \Psi(\vec{q}', -\vec{q}') \rangle.$$

With account of the symmetry of the ns^2 -configuration [7] the following solutions of (21) can be written:

$$f(\Omega) = Y_{LM}(\theta, \varphi). \quad (22)$$

In other words, for the ns^2 -configuration with shifted shells the set of orthogonal states can be introduced:

$$\tilde{\Psi}_{LM} = N_{LM} \int Y_{LM}(\Omega) \Psi(\vec{q}, -\vec{q}) d\Omega, \quad (23)$$

the terms of which transform according to irreducible representations of the rotation group. These states could be called the dynamic ones, as they can result in the correlational contribution to orbital current. The spectrum of these states can be not similar to that of the space rotator. Note that for such states with the dynamic shifts of the electronic shells one might expect the anomalously large values of the electric (dipole, quadrupole) or magnetic susceptibilities, and these values reflect the electronic correlation effects.

6 The MO-LCAO-scheme with the shifted atomic orbitals

Introduction of the shifted one-electron atomic orbitals implies the generalization of the conventional MO-LCAO-scheme [8]. Instead of standart set of the molecular orbitals (MO) $\varphi_{\Gamma_0\gamma_0}(\vec{r}, 0)$ being the symmetrized combination of the atomic functions centered in the points of the equilibrium nuclei positions ($\vec{q}_{\Gamma\gamma} = 0$), the new set of the shifted MO:

$$\varphi_{\Gamma_0\gamma_0}(\vec{r}, \vec{q}_{\Gamma\gamma}) = \hat{T}_{\vec{q}_{\Gamma\gamma}} \varphi_{\Gamma_0\gamma_0}(\vec{r}, 0), \quad (24)$$

should be introduced, where $\vec{q}_{\Gamma\gamma}$ is the symmetrized coordinate of the atomic orbital displacements in cluster, $\hat{T}_{\vec{q}_{\Gamma\gamma}}$ the operator of the symmetrized displacement. Such an approach is the natural generalization of the shifted electronic

shells model for the many-atomic cluster. The symmetry group of the wave function (24) is an intersection of the group germs of the Γ_0 and G . In contrast with the symmetrized coordinates of the cluster vibrations, the vector $\vec{q}_{\Gamma\gamma}$ is fixed and defines the certain distorted distribution of the electronic density. If $\Gamma \neq A_1$, then the function (24) doesn't possess the proper transformation properties or, in other words, doesn't belong to certain irreducible representation of the symmetry group for the undistorted cluster. This situation appears to be quite similar to the case of a single center, where the single electron displacement reduces the symmetry of system to the minimal one (axial).

Supposing that other things being equal the configuration minimizing the inter-electron interaction has the lowest energy, we can introduce the following two-particle wave function

$$\Psi_{\Gamma_0\gamma_0;\Gamma\gamma}(\vec{r}_1, \vec{r}_2; \vec{q}_{\tilde{\Gamma}\tilde{\gamma}}) = N (1 \pm \hat{P}_{12}) \hat{T}_{q_{\tilde{\Gamma}\tilde{\gamma}}}^{(1)} \hat{T}_{-q_{\tilde{\Gamma}\tilde{\gamma}}}^{(2)} \varphi_{\Gamma_0\gamma_0}(\vec{r}_1, 0) \varphi_{\Gamma_0\gamma_0}(\vec{r}_2, 0), \quad (25)$$

where N is the normalization factor, \hat{P}_{12} is the electron permutation operator, $\hat{T}_{q_{\tilde{\Gamma}\tilde{\gamma}}}^{(i)}$ is the operator of the symmetrized displacement $q_{\tilde{\Gamma}\tilde{\gamma}}$ which transforms accordingly to irreducible representation $\tilde{\Gamma}\tilde{\gamma}$ and operates in the space of the i th electron coordinates. The upper sign corresponds to the singlet wave function, the lower sign to the triplet one. The transformational properties $\Gamma\gamma$ of the two-particle wave function (25) are defined by $\Gamma\gamma = \Gamma_0\gamma_0 \times [\tilde{\Gamma}\tilde{\gamma}]^2$ for the singlet, and $\Gamma\gamma = \Gamma_0\gamma_0 \times \tilde{\Gamma}\tilde{\gamma}$ for the triplet.

7 Electronic Jahn-Teller effect

Non-rigid shell model gives a simple and obvious example of a local pairing within the two-electron ns^2 -like configurations to be a result of the correlation effects. The local pairing is promoted by the presence of a strongly polarized shell, as well as the orbital degeneracy or quasi-degeneracy within valent states (for simplicity, d -states) through the electric multipole s - d -interaction described by the effective "vibronic-like" Hamiltonian

$$V^{sd} = \sum_{\gamma} B_{\gamma} \langle \hat{V}^{\gamma} q^{\gamma} \rangle,$$

where the \hat{V}^{γ} operator works within d -manifold, the B_{γ} are "vibronic-like" parameters. This interaction can result in a purely electronic Jahn-Teller effect.

In general, one has to take account of the atomic displacements Q^{γ} modes and

their interaction with electronic q^γ shifts:

$$V_{qQ} = \sum_{\gamma} b_{\gamma} \langle Q^{\gamma} q^{\gamma} \rangle.$$

This results in a complicated multi-mode Jahn-Teller effect with a correlational hybridization at the s -, d -electron modes and the local structural modes.

This system will have all anomalous properties of a Jahn-Teller center, in particular, large values of the low-frequency polarizability. It appears that within the non-rigid shell model the completely filled electron shells do not quench and can reveal many peculiarities similar to the nonfilled shells. The magnitudes of the shell q^γ shifts are correlation parameters which may be found by minimizing the energy functional $E(q)$. The quantity $\Delta = E(0) - E(q_0)$ determines the pairing energy, i.e., the local boson binding energy.

Non-rigid shell model can be considered to be a generalization of the well known shell model of the lattice dynamics and of the non-rigid anionic background model by J.E.Hirsch et al. [9]. In particular, a correlational pseudospin formalism can be successfully applied for a description of the valent states for the atomic systems with a correlational near degeneracy. Finally, we would like to conjecture the possible importance of the non-rigid shells correlation effects for a local pairing in copper oxides.

8 Non-rigid shell model and hyperfine coupling

A correlational shift of the one-electron shells could result in a considerable renormalization of the hyperfine coupling both for the nominally ns - and non- s -orbitals. Here we consider only two effects:

- 1) an appearance of the effective non- s -contribution to contact hyperfine coupling, and
- 2) an appearance of the effective nuclear quadrupole interactions for the nominally ns -electrons.

Firstly, a shift of the one-electron non- s -shells for two-electron configuration implies an emergence of the effective electron density on the nucleus and could be detected in nuclear resonance, first of all in anomalous isotope (chemical) shift. In other words, the bare p -, d -, ... electrons within the non-rigid shell configurations appear to be involved in the contact hyperfine coupling.

Secondly, a shift of the one-electron shells for two-electron configuration results in a modification of the nuclear quadrupole coupling due to change in

the electric field gradient. Moreover, breaking the spherical symmetry of the electron density distribution within the ns^2 configurations with the shifted shells leads to an appearance of the electric field gradient on the nucleus:

$$V_{ij} \propto q_i q_j - \frac{1}{3} \bar{q}^2 \delta_{ij}.$$

The effects under consideration could provide real opportunities for a detection of the correlational shift of the one-electron shells with the help of various nuclear methods.

9 Conclusion

In a framework of the non-rigid shell model a correlated state of two-electron molecular configuration is described by a set of symmetrized shell shifts q^γ similarly to the well known shell model developed for a description of the lattice dynamics. Such a state could appear even for the completely filled shells thus resulting in a non-rigid atomic background with internal degrees of freedom. Contrary to conventional approach this background in common has nonzero electric and magnetic multipole moments. Non-rigid shell/background model results in a number of the novel unconventional effects including: i) a correlational mechanism of the local pairing; ii) a correlational (pseudo) Jahn-Teller effect provided by a joint account of the electron shell shifts and conventional nuclear displacements; iii) an appearance of the correlational current states. The model allows an introduction of the pseudo-spin formalism and effective "spin-Hamiltonian" for a description of the short- and long-range ordering of the non-rigid atomic backgrounds in crystals. Finally, the model can be readily built in the conventional band schemes.

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Appendix

Here are expressions of the matrix elements with a single-particle state

$$\psi_k(\vec{r}) = N_{Z,k} r^k e^{-Zr}, \quad \text{where } N_{Z,k} = \frac{(2Z)^{k+\frac{3}{2}}}{\sqrt{4\pi(2k+2)!}}$$

are presented.

The matrix element of kinetic energy of electron with functions of the same center is:

$$t(\vec{\alpha}, \vec{\alpha}) = \int d\vec{r} \psi_k(\vec{r}) \left(-\frac{\Delta}{2}\right) \psi_k(\vec{r}) = \frac{Z^2}{2(2k+1)} \quad (26)$$

The matrix element of interaction of electron with the potential center with functions of the same center is:

$$\begin{aligned} u(\vec{\alpha}, \vec{\alpha}) &= \int \frac{d\vec{r}}{r} \psi_k^2(\vec{r} - \vec{\alpha}) \\ &= Z \left[\frac{1}{\tilde{\alpha}} - \frac{e^{-2\tilde{\alpha}}}{\tilde{\alpha}} \sum_{l=0}^{2k+1} \left(1 - \frac{l}{2k+2}\right) \frac{(2\tilde{\alpha})^l}{l!} \right], \end{aligned} \quad (27)$$

where $\tilde{\alpha} = Z\alpha$.

The overlap integral for the one-particle orbitals is:

$$S(\vec{\alpha}, \vec{\beta}) = \int d\vec{r} \psi_k(\vec{r} - \vec{\alpha}) \psi_k(\vec{r} - \vec{\beta}) = \frac{e^{-\rho}}{(2k+2)!} \sum_{s=0}^{2k+2} C_s^{(k,k)} \rho^s, \quad (28)$$

where $\rho = Z|\vec{\alpha} - \vec{\beta}|$,

$$A_j^{(n,n')} = \sum_{l=\max\{0, 2j-n-1\}}^{\min\{2j, n'+1\}} (-1)^l \binom{n+1}{2j-1} \binom{n'+1}{l}, \quad \binom{a}{b} = \frac{a!}{b!(a-b)!};$$

$$C_s^{(n,n')} = \sum_{j=0}^{\left[\frac{s}{2}\right]} \frac{A_j^{(n,n')}}{2j+1} \frac{(n+n'+2-2j)!}{(s-2j)!}, \quad \text{where } \left[\frac{s}{2}\right] - \text{integer of } s/2,$$

$$\text{defined by } \frac{2^{n+n'+3}}{4\pi} \int d\vec{x} |\vec{x} - \vec{\alpha}|^n e^{-|\vec{x}-\vec{\alpha}|} |\vec{x} - \vec{\beta}|^{n'} e^{-|\vec{x}-\vec{\beta}|} = e^{-\rho} \sum_{s=0}^{n+n'+2} \rho^s C_s^{(n,n')}.$$

The matrix element of kinetic energy of electron with functions of different centers is:

$$\begin{aligned}
t(\vec{\alpha}, \vec{\beta}) &= \int d\vec{r} \psi_k(\vec{r} - \vec{\alpha}) \left(-\frac{\Delta}{2} \right) \psi_k(\vec{r} - \vec{\beta}) \\
&= -Z^2 \frac{e^{-\rho}}{2(2k+2)!} \left[\sum_{s=0}^{2k+2} \rho^s C_s^{(k,k)} - 4(k+1) \sum_{s=0}^{2k+1} \rho^s C_s^{(k,k-1)} \right. \\
&\quad \left. + 4k(k+1) \sum_{s=0}^{2k} \rho^s C_s^{(k,k-2)} \right],
\end{aligned} \tag{29}$$

The matrix element of Coulomb part of inter-electron interaction is:

$$\begin{aligned}
c(\vec{\alpha}, \vec{\beta}) &= \int \frac{d\vec{r}_1 d\vec{r}_2}{|\vec{r}_1 - \vec{r}_2|} \psi_k^2(\vec{r}_1 - \vec{\alpha}) \psi_k^2(\vec{r}_2 - \vec{\beta}) \\
&= Z \left[\frac{1}{\rho} - \frac{e^{-2\rho}}{(2k+2)\rho} \sum_{l=0}^{2k+1} \rho^l \frac{2^l (2k+2-l)}{l!} \right. \\
&\quad \left. - \frac{e^{-2\rho}}{2^{2k+2}(k+1)(2k+2)!} \sum_{l=0}^{4k+2} \rho^l G_l^{(k)} \right],
\end{aligned} \tag{30}$$

where

$$G_l^{(k)} = 2^l \sum_{j=\max\{0, l-2k-1\}}^{2k+1} \frac{(2k+2-j)}{2^j j!} C_l^{(2k, j-1)}.$$

The matrix element of exchange part of inter-electron interaction is:

$$\begin{aligned}
a(\vec{\alpha}, \vec{\beta}) &= \int \frac{d\vec{r}_1 d\vec{r}_2}{|\vec{r}_1 - \vec{r}_2|} \psi_k(\vec{r}_1 - \vec{\alpha}) \psi_k(\vec{r}_2 - \vec{\beta}) \psi_k(\vec{r}_1 - \vec{\beta}) \psi_k(\vec{r}_2 - \vec{\alpha}) \\
&= Z \frac{\rho^{4k+5}}{[(2k+2)!]^2} \sum_{s=0}^{k+1} (4s+1) \sum_{n=0}^{2k+2} \rho^n F_{s,n}^{(k+1)}(\rho) \left\{ e^{-\rho \Sigma_{s,0}^{(k+1)}}(\rho) - \Sigma_{s,n}^{(k+1)}(2\rho) \right\},
\end{aligned} \tag{31}$$

where

$$\begin{aligned}
F_{s,n}^{(m)}(\rho) &= \frac{1}{n!} \sum_{j=\frac{n+1}{2}}^m B_j^{(m,s)} \frac{(2j)!}{\rho^{2j+1}}; \quad B_j^{(m,s)} = \sum_{r=\max\{0, j-s\}}^{\min\{j, m-s\}} a_r^{(m,s)} b_{j-r}^{(s)}; \\
\Sigma_{s,n}^{(m)}(x) &= \tilde{\Sigma}_{s,n}^{(m)}(x) - \frac{e^{-x}}{x^{n+2}} \tilde{\Sigma}_{s,n}^{(m)}(x, 1); \\
\tilde{\Sigma}_{s,n}^{(m)}(x, \xi) &= \sum_{i=0}^{m-1} \frac{(2i+n+1)!}{x^{2i}} \tilde{D}_i^{(m,s)} \sum_{t=0}^{2i+n+1} \frac{(x\xi)^t}{t!};
\end{aligned}$$

$$\begin{aligned}
\tilde{\Sigma}_{s,n}^{(m)}(x) &= \frac{e^{-x}}{2x} \sum_{i=0}^{m-s} a_i^{(m,s)} \times \\
&\times \sum_{l=0}^{2s+2i+n} \frac{\sigma_{2i+n,l}^{(s)}(1)}{x^l} \left[\ln 2\gamma x - S_{0,l} - (-1)^{l+n} e^{2x} Ei(-2x) + (-1)^{l+n} \sum_{h=0}^{l-1} \frac{(2x)^h}{h!} S_{h,l} \right], \\
\tilde{D}_i^{(m,s)} &= \sum_{l=\max\{0, i-s+1\}}^{\min\{i, m-s\}} a_l^{(m,s)} D_{i-l}^{(s)}; \quad \sigma_{t,l}^{(s)}(\xi) = \sum_{r=\max\{0, \frac{l-t+1}{2}\}}^s b_r^{(s)} \frac{(2r+t)!}{(2r+t-l)!} \xi^{2r+t}; \\
S_{h,l} &= \sum_{t=h+1}^l \frac{1}{t}; \quad a_l^{(m,s)} = (-1)^{m-l} \binom{m}{l} \frac{2^{2s+2} (2m-2l)! (m-l+s+1)!}{(m-l-s)! (2m-2l+2s+2)!} \\
&- \text{the coefficients in } \sum_{l=0}^m a_l^{(m,s)} x^l = \int_{-1}^1 (x^2 - t^2)^m P_{2s}(t) dt; \\
&\text{the coefficients } b_l^{(s)} \text{ and } D_l^{(s)} \text{ define the Legendre polynomial } P_{2s}(x): \\
P_{2s}(x) &= \sum_{l=0}^s b_l^{(s)} x^{2l}, \quad b_l^{(s)} = \frac{(-1)^{s-l}}{2^{2s}} \frac{(2s+2l)!}{(s-l)! (s+l)! (2l)!}, \\
&\text{and the Legendre polynomial of second type } Q_{2s}(x): \\
Q_{2s}(x) &= \frac{1}{2} \ln \frac{x+1}{x-1} P_{2s}(x) - \sum_{l=0}^{s-1} D_l^{(s)} x^{2l+1}; \\
D_l^{(s)} &= \frac{(-1)^l}{(2l+1)!} \sum_{t=l}^{s-1} \frac{(-1)^t (4t+3)(2t+2l+2)!}{2^{2t+1} (2s-2t-1)(s+t+1)(t-l)!(t+l+1)!}; \\
\gamma &= 1.78107; \quad Ei(x) - \text{the exponential integral function [1];} \\
\xi &= \frac{\alpha + \beta}{|\vec{\alpha} - \vec{\beta}|}, \quad \eta = \frac{\alpha - \beta}{|\vec{\alpha} - \vec{\beta}|}.
\end{aligned}$$

The matrix element of interaction of electron with the potential center with functions of different centers is:

$$\begin{aligned}
u(\vec{\alpha}, \vec{\beta}) &= \int \frac{d\vec{r}}{r} \psi_k(\vec{r} - \vec{\alpha}) \psi_k(\vec{r} - \vec{\beta}) \\
&= Z \frac{\rho^{2k+2}}{(2k+2)!} \sum_{s=0}^{k+1} (4s+1) P_{2s}(\eta) \left\{ Q_{2s}(\eta) \sum_{n=0}^{2k+2} [e^{-\rho} \rho^n - e^{-\rho\xi} (\rho\xi)^n] F_{s,n}^{(k+1)}(\rho) \right. \\
&\quad - P_{2s}(\xi) \frac{e^{-\rho\xi}}{\rho^2} \tilde{\Sigma}_{s,0}^{(k+1)}(x, \xi) + \frac{P_{2s}(\xi)}{2} \sum_{i=0}^{k+1-s} a_i^{(k+1,s)} \left[\ln \frac{\xi+1}{\xi-1} \cdot \frac{e^{-\rho\xi}}{\rho} \sum_{l=0}^{2s+2i} \frac{\sigma_{2i,l}^{(s)}(\xi)}{(\rho\xi)^l} \right. \\
&\quad \left. + \sum_{l=0}^{2s+2i} \frac{\sigma_{2i,l}^{(s)}(1)}{\rho^{l+1}} \left((-1)^{l+1} e^{\rho} Ei(-\rho(\xi+1)) + e^{-\rho} Ei(-\rho(\xi-1)) \right) \right. \\
&\quad \left. \left. - e^{-\rho\xi} \sum_{h=0}^{l-1} \frac{\rho^h}{h!} S_{h,l} \left((-1)^{l+1} (\xi+1)^h + (\xi-1)^h \right) \right] \right\}.
\end{aligned} \tag{32}$$

Tables

Table 1. The results of numerical minimization of the full energy functional for the $1s^2$ -configuration ($k = 0$) at $Z = Z_0$.

Z	α	β	φ	$E(\vec{\alpha}, \vec{\beta})$
1.5	0.078	0.078	3.1415	-1.3140
1.6	0.068	0.068	3.1415	-1.5614
1.7	0.059	0.059	3.1415	-1.8287
1.8	0.051	0.051	3.1415	-2.116
1.9	0.046	0.046	3.1415	-2.4236
2.0	0.043	0.043	3.1415	-2.7510
2.1	0.041	0.041	3.1415	-3.0984
2.2	0.038	0.038	3.1415	-3.4658
2.3	0.036	0.036	3.1415	-3.8533
2.4	0.034	0.034	3.1415	-4.2608
2.5	0.033	0.033	3.1415	-4.6882

Table 2. The results of numerical minimization of the full energy functional for the $1s^2$ -configuration ($k = 0$) at $Z_0 = 2.0$.

Z	α	β	φ	$E(\vec{\alpha}, \vec{\beta})$
1.5	0.0	0.0	—	-2.8125
1.6	0.0	0.0	—	-2.8400
1.7	0.0	0.0	—	-2.8475
1.8	0.0	0.0	—	-2.8350
1.9	0.011	0.011	3.1415	-2.8026
2.0	0.043	0.043	3.1415	-2.7510
2.1	0.065	0.065	3.1415	-2.6809
2.2	0.084	0.084	3.1415	-2.5931
2.3	0.102	0.102	3.1415	-2.4877
2.4	0.118	0.118	3.1415	-2.3650
2.5	0.132	0.132	3.1415	-2.2253

Table 3.

q -expansion of the matrix elements up to q^2 .

General expression	q -expansion up to q^2
$S(\vec{q}, -\vec{q}) \approx 1 - q^2 \int d\vec{r} b^2$	$1 - q^2 \frac{2Z^2}{3(2k+1)}$
$t(\vec{q}, \vec{q}) = -\frac{1}{2} \int d\vec{r} a \Delta a$	$\frac{Z^2}{2(2k+1)}$
$u(\vec{q}, \vec{q}) \approx \int \frac{d\vec{r}}{r} a^2 + q^2 \int \frac{d\vec{r}}{r} (b^2 + a c)$	$Z - q^2 \frac{2Z^3}{3}, \quad k = 0$ $\frac{Z}{k+1}, \quad k \neq 0$
$t(\vec{q}, -\vec{q}) \approx -\frac{1}{2} [\int d\vec{r} a \Delta a + q^2 \int d\vec{r} c \Delta a]$	$\frac{Z^2}{2} - q^2 \frac{5Z^4}{3}, \quad k = 0$ $\frac{Z^2}{2(2k+1)} - q^2 \frac{Z^4}{4k^2-1}, \quad k \neq 0$
$u(\vec{q}, -\vec{q}) \approx \int \frac{d\vec{r}}{r} a^2 + q^2 \int \frac{d\vec{r}}{r} (-b^2 + a c)$	$Z - q^2 \frac{4Z^3}{3}, \quad k = 0$ $\frac{Z}{k+1} - q^2 \frac{2Z^3}{3(2k+1)(k+1)}, \quad k \neq 0$
$c(\vec{q}, -\vec{q}) \approx \int \frac{d\vec{r}_1 d\vec{r}_2}{r_{12}} a_1^2 a_2^2 +$ $+ q^2 \int \frac{d\vec{r}_1 d\vec{r}_2}{r_{12}} (-2a_1 b_1 a_2 b_2 + a_1^2 b_2^2 + a_1^2 a_2 c_2)$	$Z \left(\frac{1}{k+1} - \frac{(4k+3)!}{2^{4k+2} [(2k+2)!]^2} \right) -$ $- q^2 Z^3 \frac{(4k+2)!}{3 \cdot 2^{4k-1} [(2k+2)!]^2}$
$a(\vec{q}, -\vec{q}) \approx \int \frac{d\vec{r}_1 d\vec{r}_2}{r_{12}} a_1^2 a_2^2 +$ $+ q^2 \int \frac{d\vec{r}_1 d\vec{r}_2}{r_{12}} (-a_1^2 b_2^2 + a_1^2 a_2 c_2)$	$Z \left(\frac{1}{k+1} - \frac{(4k+3)!}{2^{4k+2} [(2k+2)!]^2} \right) +$ $+ q^2 Z^3 \left(-\frac{4}{3(2k+1)(k+1)} + \frac{(4k+2)!}{3 \cdot 2^{4k-1} [(2k+2)!]^2} \right)$
$E^{(0)} = -\int d\vec{r} a \Delta a - 2Z_0 \int \frac{d\vec{r}}{r} a^2 +$ $+ \int \frac{d\vec{r}_1 d\vec{r}_2}{r_{12}} a_1^2 a_2^2$	$Z^2 - 2Z_0 Z + \frac{5}{8} Z, \quad k = 0$ $\frac{Z^2}{2k+1} - \frac{2Z Z_0}{k+1} +$ $+ Z \left(\frac{1}{k+1} - \frac{(4k+3)!}{2^{4k+2} [(2k+2)!]^2} \right), \quad k \neq 0$
$E^{(2)} = -\int d\vec{r} c \Delta a - \int d\vec{r} a \Delta a \int d\vec{r} b^2 -$ $- 2Z_0 \left(\int \frac{d\vec{r}}{r} a c + \int \frac{d\vec{r}}{r} a^2 \int d\vec{r} b^2 \right) +$ $+ 2 \int \frac{d\vec{r}_1 d\vec{r}_2}{r_{12}} [a_1^2 a_2 c_2 - a_1 b_1 a_2 b_2 + a_1^2 a_2^2 \int d\vec{r} b^2]$	$-\frac{4Z^3}{3} \left(Z - Z_0 + \frac{3}{16} \right), \quad k = 0$ $- Z^4 \frac{4(k+1)}{3(4k^2-1)} -$ $- Z^3 \frac{(4k+3)!}{3 \cdot 2^{4k+1} (2k+1) [(2k+2)!]^2}, \quad k \neq 0$

Here $r_{12} = |\vec{r}_1 - \vec{r}_2|$, and the index i of the functions a, b, c indicates dependence on \vec{r}_i .

Table 4.

k	E_{min}	q_{min}	Z_{min}	$E_{min}(q=0) - E_{min}$	$Z_{min}(q=0) - Z_{min}$
0	-2.84766	0.0	1.6875	0	0
1	-2.22965	0.3437	2.7110	0.2205	-0.2559
2	-1.79140	0.5061	3.2084	0.3463	-0.5204
3	-1.48131	0.6385	3.4999	0.3638	-0.7030
4	-1.25036	0.7644	3.6778	0.3424	-0.8192

Figures

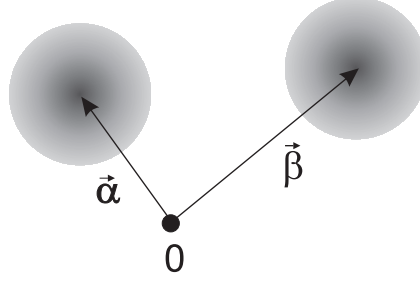


Fig. 1. The displacement vectors $\vec{\alpha}$ and $\vec{\beta}$ define the centers of the one-particle orbitals relative to the potential center.

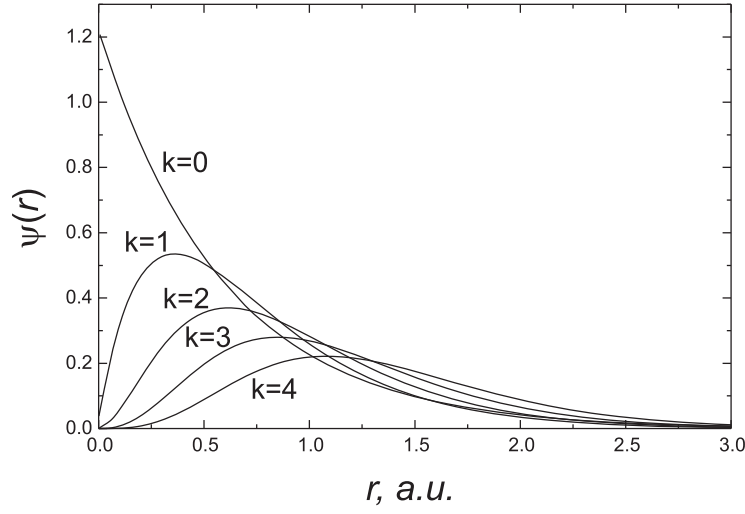


Fig. 2. The Slater orbitals $\psi(r)$ (6) at $Z = Z_{min}^{(k)}$.

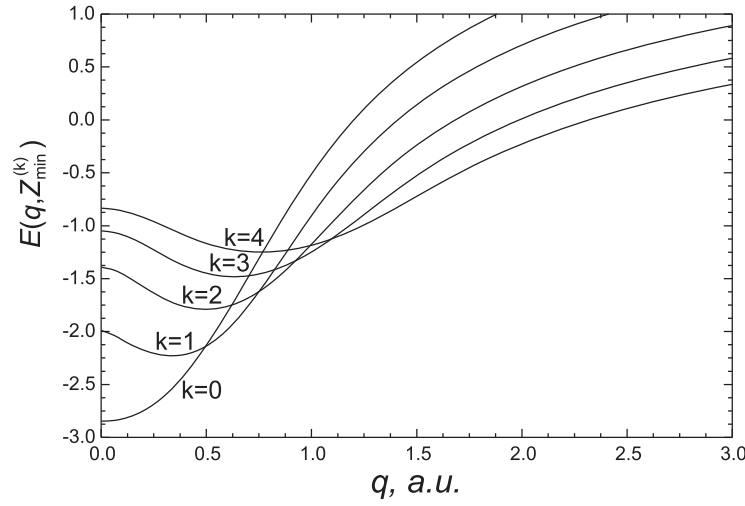


Fig. 3. The full energy functional $E(q, Z)$ at $Z = Z_{min}^{(k)}$.

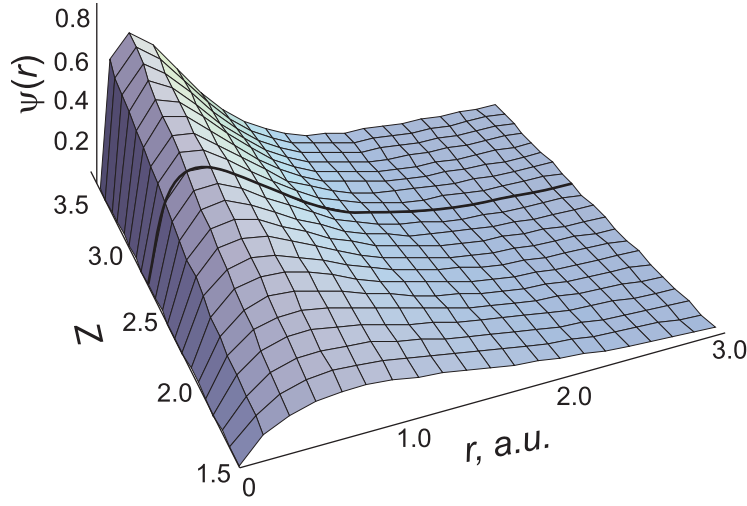


Fig. 4. The variation of the form of the one-particle function $\psi(r)$ at $k = 1$ with variation in Z . The bold line corresponds to $Z = Z_{min}^{(1)}$.

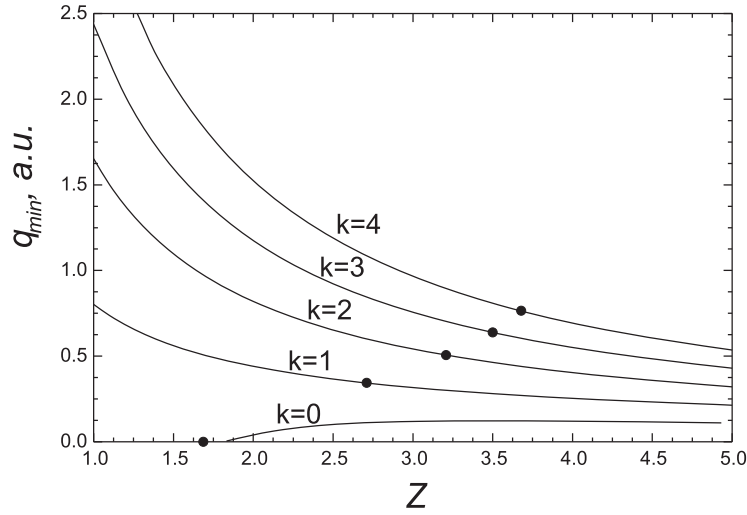


Fig. 5. The value of the electronic shell displacement q minimizing the full energy as function of the given parameter Z . The points correspond to minimal values of the full energy at the given k .

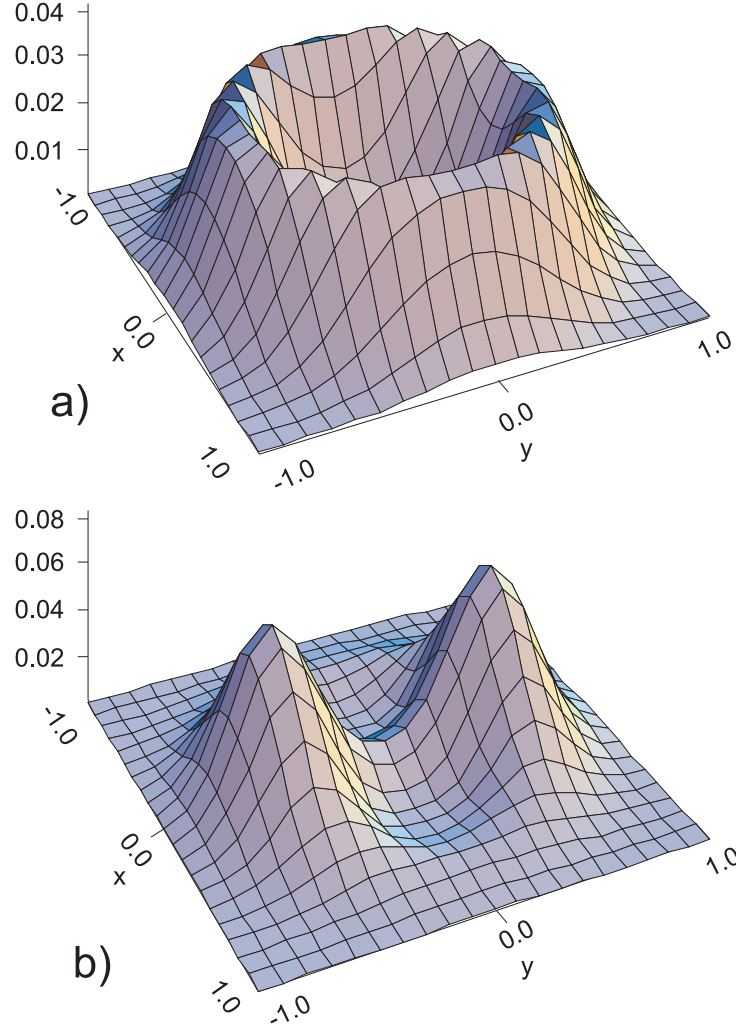


Fig. 6. The two-electron density distribution in plane $z = 0$ for the state $\Psi(\vec{r}_1, \vec{r}_2; \vec{q}, -\vec{q})$, $k = 1$, $Z_0 = 2$ a) without shifts of the electronic shells ($Z = Z_{min}^{(1)}$ at $\vec{q} = 0$); b) with shifts $Z = Z_{min}^{(1)}$, $\vec{q} = (q_{min}^{(1)}, 0, 0)$.